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MOLECULAR ELECTRONIC PHOTODISSOCIATION LASER STUDIES.(U)
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Abstract

Chemical laser experimental techniques were used to analyze features of energy partitioning and electronic branching in photochemical and bimolecular chemical reactions. Accurate population inversions were determined for two classes of reactions: 1) photodissociation (e.g., photodissociative excitation of cyanide radical by photolysis of CH_3NC) and 2) bimolecular exchange [e.g., $\text{F} + \text{HI} \rightarrow \text{HF}^+(\text{v}) + \text{I}$]. New lasing transitions of the cyanide radical molecular electronic laser were obtained. In addition, energy redistribution processes were examined in the cyanide radical laser system.

Support and screening experiments in areas of vacuum ultraviolet spectroscopy and fluorescence quantum yield measurements were completed at the University of Wisconsin Synchrotron Radiation Facility.

Certain theoretical work was performed to determine dynamical features that govern vibronic population distributions in photochemical reactions. Information theoretic analyses and computations based upon a Franck-Condon model of intra-fragment dynamics showed that the structural change of a diatomic fragment in evolving from reactant to photochemical product is the dominant factor that produces observed vibronic state distributions. Analyses of related reaction examples (collisional dissociative excitation and electronic-to-vibrational energy transfer) were also carried out.

The following report details the above and other accomplishments of our work supported by the Air Force Office of Scientific Research.

I. Project Goals

We analyze published and unpublished work in the context of program goals as summarized from original (first-year) plus renewal proposals:

- 1) quantitative determination of product energy content resulting from bimolecular and photochemical reactions
- 2) vacuum ultraviolet absorption spectroscopy and photochemical reaction product fluorescence measurements
- 3) development of new sub-microsecond flash photolysis equipment
- 4) theoretical approaches toward reaction dynamics
- 5) discovery of new chemical laser systems (particularly electronic chemical lasers).

Substantial successes were obtained in meeting and exceeding goals 1, 2, and 4. Working apparatus was constructed and operated for goal 3, but detailed experiments were not completed. Several attempts to meet goal 5 were unsuccessful.

II. Summary of Accomplishments

In the following subsections, published papers are referenced according to the numbering sequence used in the Chronological Bibliography contained in Section V at the end of this report.

A) Quantitative Determination of Energy Partitioning

We used a grating-tuned laser cavity technique to analyze features of energy partitioning in two classes of chemical reactions: 1) photodissociation of CH_3NC at $\lambda > 1550 \text{ \AA}$ - (References 3-4) and 2) bimolecular exchange [e.g., $\text{F} + \text{HI} \rightarrow \text{HF}^+(v) + \text{I}$] - (S. N. Bittenson, Ph.D. thesis, in preparation). For CH_3NC photodissociation, we determined that $\text{CN}^*(A^2\Pi, v=0)$ is the predominant nascent photochemical product (>80%) and that spin-orbit and rotational relaxation are rapid processes on present chemical laser emission timescales. For hydrogen and deuterium exchange reactions, we determined complete vibronic population inversions of all the hydrogen and deuterium halide products. Curved surprisal plots in the $\text{F} + \text{HI}$ and $\text{F} + \text{DI}$ systems indicate that electronically excited iodine atoms may be formed chemically with moderate efficiency.

B) Synchrotron Radiation Experiments

We used our automated absorption and fluorescence spectroscopy apparatus at the University of Wisconsin Synchrotron Radiation Facility to determine relative fluorescence quantum yields for production of $\text{CN}^*(A^2\Pi)$ and $\text{CN}^*(B^2\Sigma)$ by photolysis of cyanide radical parents [G. A. West, Ph.D. thesis, University of Wisconsin, 1975 (copy sent to AFOSR)].

C) Development of Sub-Microsecond Flash Photolysis Equipment

We constructed a chemical laser apparatus incorporating a linear array of five flashlamps to produce a fast (ca. 200 nsec risetime), high intensity (500 - 600J stored electrical energy) photolysis source for screening of potential

molecular electronic chemical lasers. Many known chemical laser systems (I^* , CN^* , etc.) operated readily in this device, but searches for new chemical lasers were unsuccessful (S. Bittenson, Ph.D. thesis, in preparation).

D) Theoretical Approaches Toward Reaction Dynamics

We used information theoretic analyses to understand the distribution of vibronic states produced in photodissociation, predissociation, and collision-induced dissociative excitation reactions and in electronic-to-vibrational energy transfer (Reference 1). Franck-Condon model computations were performed on several reaction and relaxation systems that yield electronically excited products (Reference 2).

E) Discovery of New Chemical Lasers

Numerous attempts to produce new electronic chemical lasers on systems such as C_2H^* (formed by photodissociation of $RC\equiv CH$ compounds) and SnO^* (formed as a product of the $Sn + N_2O$ bimolecular reaction) were all unsuccessful (K. V. Reddy, Ph.D. thesis, in preparation).

F) Other Accomplishments

We constructed a chemical laser apparatus incorporating a coaxial flashlamp equipped with MgF_2 windows for extension of flash photolysis capabilities down to ca. 1200 Å. High-gain chemical laser emission was obtained on HF produced by photolysis of SF_6 in SF_6/H_2 mixtures (K. V. Reddy, Ph.D. thesis, in preparation).

III. Personnel Supported and Degrees Completed

Eight graduate students and two postdoctoral associates have benefitted from AFOSR research support:

A) Postdoctoral Associates

Dr. Oded Kafri

Professor J. Thomas Knudtson

B) Doctoral Degree Recipients

Dr. Daniel E. Klimek

Dr. Gary A. West

C) Doctoral Candidates

Mr. Sherwin T. Amimoto

Mr. Steven N. Bittenson

Mr. Robert L. Gaither

Mr. Robert J. Gill

Mr. Kammalathinna V. Reddy

D) Master's Degree Recipient

Mr. Stephen K. Liu

IV. Presentations on AFOSR-Related Projects

A) Grant Period (2/1/74 - 1/31/76)

- 1) 1st Summer Colloquium on Electronic Transitions Lasers, Santa Barbara, California, June 18, 1974 - "Golden Rule Calculation of Reaction Product Vibronic State Distributions."
- 2) Dynamics of Molecular Collisions Conference, Santa Cruz, California, July 29 - August 1, 1974 (2 presentations):
 - a) "Energy Disposal and Energy Requirements in Polyatomic Bimolecular Reactions Systems."
 - b) "Ramifications of Vibronic Reaction Surprisals."
- 3) Departmental Seminar, Department of Chemistry, University of Texas, Austin, Texas, August 9, 1974 - "Chemical Laser Studies of Photochemistry."
- 4) Gordon Research Conference on Atomic and Molecular Interactions, Wolfeboro, New Hampshire, August 16, 1974 - "Decays of Resonances."
- 5) Conference on Radiationless Processes, Schliersee, Bavaria, West Germany, September 12, 1975 - "Photodissociative and Predissociative Excitation of the Cyanide Radical."
- 6) Physical Chemistry Seminar, Department of Chemistry, University of Minnesota, Minneapolis, MN, September 30, 1974 - "Chemical Laser Studies of Photochemical Reaction Dynamics."
- 7) 4th Conference on Chemical and Molecular Lasers, St. Louis, MO, October 21, 1974 - "Cyanide Radical Photodissociation and Predissociation Chemical Lasers: Molecular Electronic and Vibrational Laser Emissions" (with G. A. West).
- 8) Franck Colloquium, James Franck Institute, University of Chicago, Chicago, IL, November 19, 1974 - "Non-Statistical (i.e., Dynamical) Effects in Unimolecular and Photochemical Reactions."

- 9) Chemistry Seminar, Department of Chemistry, University of Illinois, Chicago, IL, November 26, 1974 - "Chemical Laser Studies of Photochemistry."
- 10) American Physical Society Division of Electron and Atomic Physics, Chicago, IL, December 4, 1974 - "Time- and Wavelength-Resolved Spectra of Pulsed Chemical Lasers."
- 11) 5th Winter Colloquium on Quantum Electronics, Snowmass, Colorado, February 4, 1975 - "CN Molecular Electronic Chemical Lasers."
- 12) AFOSR Contractor's Meeting, Kirtland AFB, New Mexico, June 3, 1975 - "Cyanide and Other (Potential) Molecular Electronic Chemical Lasers."
- 13) ACS National Meeting, Chicago, IL, August 27, 1975 - "Cyanide Radical Molecular Electronic Chemical Lasers: Grating Selection Measurements of Electronic Population Inversions" (with J. T. Knudtson).
- 14) Department of Chemistry Colloquium, Case Western Reserve University, Cleveland, Ohio, September 11, 1975 - "HCN Polyatomic Chemical Laser."
- 15) Second Summer Colloquium on Electronic Transition Lasers, Woods Hole, Massachusetts, September 19, 1975 - "Cyanide Radical Molecular Electronic Chemical Lasers: Grating Selection Measurement of Electronic Population Inversions" (with J. T. Knudtson).
- 16) Department of Chemistry Colloquium, Brown University, Providence, RI, September 19, 1975 - "HCN Polyatomic Chemical Laser."
- 17) Joint Chemistry Colloquium, Departments of Chemistry, Harvard University and MIT, Cambridge, Massachusetts, October 23, 1975 - "Dynamics of the $\text{CN} + \text{H}_2$ Reaction."

B) Post-Grant Period (after 2/1/76)

- 18) Physical Chemistry Seminar, Wayne State University, Detroit, Michigan, February 5, 1976 - "Dynamics of the $\text{CN} + \text{H}_2$ Reaction."

- 19) Physical Chemistry Seminar, Department of Chemistry, University of Illinois, Urbana, IL, April 14, 1976 - "Chemical Laser and Other Studies of $\text{CN} + \text{H}_2$ Reaction Dynamics."
- 20) Physical Chemistry Seminar, Department of Chemistry, Ohio State University, Columbus, Ohio, April 26, 1976 - "Chemical Laser and Other Studies of $\text{CN} + \text{H}_2$ Reaction Dynamics."
- 21) Bell Telephone Laboratory, Murray Hill, NJ, September 22, 1976 - "Chemical Laser and Other Studies of $\text{CN} + \text{H}_2$ Reaction Dynamics."
- 22) Departmental Colloquium, Department of Chemistry, Columbia University, New York, NY, December 2, 1976 - "Chemical Laser and Other Studies of $\text{CN} + \text{H}_2$ Reaction Dynamics."
- 23) 5th Conference on Chemical and Molecular Lasers, St. Louis, MO, April 18, 1977 - "Chemical Laser Determination of Product Vibrational State Populations for the Halogen Atom + Hydrogen (Deuterium) Halide Reactions" (with S. Bittenson).

V. Chronological Bibliography and Abstracts of Publications

A) Bibliography

- 1) M. J. Berry, "Vibronic Surprisal Analysis of the Dynamics of Photodissociation and Related Reactions," Chem. Phys. Letters, 29, 323 (1974).
- 2) M. J. Berry, "Golden Rule Calculation of Product Vibronic Population Inversions in Photodissociation and Related Reactions," Chem. Phys. Letters, 29, 329 (1974).
- 3) J. T. Knudtson and M. J. Berry, "Cyanide Radical Molecular Electronic Laser: Grating Selection Determination of Population Inversions," in J. I. Steinfeld (editor), Electronic Transition Lasers MIT Press, Cambridge, MA, 1976).
- 4) J. T. Knudtson and M. J. Berry, "Methyl Isocyanide Photodissociation: Chemical Laser Determination of Energy Partitioning Into the Cyanide Radical Photochemical Product," to be submitted to J. Chem. Phys.

B) Abstracts and/or Introductions

- 1) M. J. Berry, "Vibronic Surprisal Analysis of the Dynamics of Photodissociation and Related Reactions," Chem. Phys. Letters, 29, 323 (1974).

VIBRONIC SURPRISAL ANALYSIS OF THE DYNAMICS
OF PHOTODISSOCIATION AND RELATED REACTIONS[‡]

Michael J. BERRY

Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706, USA

Received 29 July 1974

Comparisons of experimentally observed product vibronic state distributions to statistically expected distributions indicate that intrafragment dynamics have primary importance in photodissociative and predissociative excitation reactions and in collision-induced electronic-to-vibrational energy transfer processes and that collisional dissociative excitation reactions probably involve sequential 2-body interactions rather than a concerted 3-body interaction.

- 2) M. J. Berry, "Golden Rule Calculation of Product Vibronic Population Inversions in Photodissociation and Related Reactions," Chem. Phys. Letters, 29, 329 (1974).

GOLDEN RULE CALCULATION OF PRODUCT VIBRONIC POPULATION INVERSIONS
IN PHOTODISSOCIATION AND RELATED REACTIONS[☆]

Michael J. BERRY

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Received 20 August 1974

An ultrasimple reaction dynamics model successfully treats product vibronic state distributions in photodissociation and predissociation reactions and in collision-induced electronic-to-vibrational energy transfer processes. Product vibronic population inversions are determined by intrafragment dynamics (i.e., changes in bond lengths and strengths) which occur during reaction product formation.

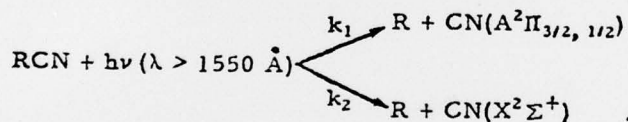
- 3) J. T. Knudtson and M. J. Berry, "Cyanide Radical Molecular Electronic Laser: Grating Selection Determination of Population Inversions," in J. I. Steinfeld (editor), Electronic Transition Lasers (MIT Press, Cambridge, MA, 1976).

III.11

CYANIDE RADICAL MOLECULAR ELECTRONIC LASER: GRATING SELECTION DETERMINATION OF POPULATION INVERSIONS

J. T. Knudtson and M. J. Berry*

The cyanide radical (CN) has a long spectroscopic and chemical kinetic history. It is readily produced in flames, electric discharges, and flash photolysis. Recently West and Berry⁽¹⁾ have reported a photodissociation and photopredissociation CN electronic laser operating in the red band system, $\text{CN}(A^2\Pi_{3/2}, v' = 0) \rightarrow \text{CN}(X^2\Sigma^+, v'' = 0, 1, 2)$ at 1.1, 1.4, and 1.9 μm . Lasing action results from a favorable branching ratio in the photodissociation process:



When $k_1/k_2 > 1$, a population inversion is produced by the photolysis of the cyanide parent compound and lasing will occur if optical gain exceeds optical loss. We have used a grating selection technique⁽²⁾ to determine the population inversion ratio produced by photolysis of CH_3NC . In addition we have observed lasing on new transitions in the previously reported $\text{CN}(A^2\Pi_{3/2}, v' = 0) \rightarrow \text{CN}(X^2\Sigma^+, v'' = 0)$ band and lasing from the (previously unreported) upper spin-orbit component of the a state, $\text{CN}(A^2\Pi_{1/2}, v' = 0) \rightarrow \text{CN}(X^2\Sigma^+, v'' = 0)$.

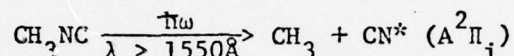
*Department of Chemistry, University of Wisconsin, Madison, Wisc. 53706. J. Thomas Knudtson is now at the Department of Chemistry, Northern Illinois University, De Kalb, Ill. 60015. Michael J. Berry is a Camille and Henry Dreyfus Foundation Teacher-Scholar, and an Alfred P. Sloan Foundation Research Fellow.

Work supported by AFOSR, Grant AFOSR-74-2666 and Contract F44620-70-C-0029, and by the University of Wisconsin Graduate School Research Committee.

- 4) J. T. Knudtson and M. J. Berry, "Methyl Isocyanide Photodissociation: Chemical Laser Determination of Energy Partitioning Into the Cyanide Radical Photochemical Product," to be submitted to J. Chem. Phys.

Abstract

Chemical laser techniques have been used to study the photodissociative excitation of cyanide radical by photolysis of methyl isocyanide:



and to identify efficient spin-orbit relaxation of cyanide radical between its $\text{A}^2\Pi_{1/2}$ and $\text{A}^2\Pi_{3/2}$ manifolds. Many new chemical laser transitions have been obtained within the cyanide radical 0,0 red band $[\text{CN}^*(\text{A}^2\Pi_1, v' = 0) \longrightarrow \text{CN}(\text{X}^2\Sigma^+, v'' = 0)]$ by selective cavity Q-spoiling with a diffraction grating. In addition, measurements of the relative gain coefficients of grating-selected laser transitions establish that photochemical reaction branching strongly favors $\text{CN}^*(\text{A}^2\Pi_1, v = 0)$ production; other possible product states [e.g., $\text{CN}^*(\text{A}^2\Pi_1, v \geq 1)$ and $\text{CN}(\text{X}^2\Sigma^+, v = 0)$] are minor components (<10%) of the nascent cyanide radical concentration. The observed cyanide radical product state distribution is highly surprising (i.e., highly non-statistical), signifying that strong dynamical effects govern the process of photodissociative excitation.

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20. Abstract (Continued)

were examined in the cyanide radical laser system.

Support and screening experiments in areas of vacuum ultraviolet spectroscopy and fluorescence quantum yield measurements were completed at the University of Wisconsin Synchrotron Radiation Facility.

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